

Zero-Temperature Structures of Atomic Metallic Hydrogen

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Abstract

Ab initio random structure searching with density functional theory was used to determine the zero-temperature structures of atomic metallic hydrogen from 500 GPa to 5 TPa. Including zero point motion in the harmonic approximation, we estimate that molecular hydrogen dissociates into a monatomic body-centered tetragonal structure near 500 GPa ($r_s = 1.225$), which then remains stable to 2.5 TPa ($r_s = 0.969$). At higher pressures, hydrogen stabilizes in an ...*ABCABC*... planar structure that is remarkably similar to the ground state of lithium, which compresses to the face-centered cubic lattice beyond 5 TPa ($r_s < 0.86$). At this level of theory, our results provide a complete ab initio description of the atomic metallic structures of hydrogen, resolving one of the most fundamental and long outstanding issues concerning the structures of the elements.

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Since the first prediction of an atomic metallic phase of hydrogen by Wigner and Huntington over 75 years ago [1], there have been many theoretical efforts aimed at determining the crystal structures of the zero-temperature phases as a function of density [2–9]. Such interest is understandable, considering the importance to astrophysics, predictions of high- T_c superconductivity [10], and the possibility of a low or even zero-temperature metallic liquid [11]. Despite the importance and corresponding efforts, there is still no conclusive understanding of this most basic and fundamental aspect. These efforts have been hindered by the fact that experiments have only been able to reach pressures of just over 300 GPa [12], which is lower than that of the atomic phase(s).

Previous studies have taken the approach of simply proposing candidate structures, leading to diverse predictions. In some cases, isotropic structures have been predicted as the ground state [2, 5, 6, 8], while in others anisotropic ones have [3, 4, 7, 9, 13, 14]. This diversity is related to the primary disadvantage of such an approach, in that only a few select structures can be considered at any one time. It is apparent that, in analogy with the other alkali metals, even an elemental solid can have a rather complex structure [15]. Recently, however, more robust methods for determining crystal structures have been proposed, such as the ab initio random structure searching (AIRSS) method by Pickard and Needs [16]. In this approach, a number of random configurations are each relaxed to the ground state at constant pressure. After enough trials, a good sampling of the atomic configuration space is obtained and the ground state structure is generated with a high probability. Such an approach has been used to accurately predict a number of structures, including more complicated ones than considered here, such as silane [16] and the highest pressure molecular phase of hydrogen, phase III [17].

In this Letter, we use AIRSS to determine the zero-temperature structures of atomic metallic hydrogen. Our calculations were performed using the Quantum Espresso ab initio density functional theory (DFT) code [18]. A norm-conserving Troullier–Martins pseudopotential [19] with a cutoff radius of 0.5 a.u. was used to replace the true $1/r$ Coulomb potential of hydrogen, along with the Perdew, Burke, and Ernzerhof exchange and correlation functional [20]. A basis set of plane-waves with a cutoff of 2721 eV was used for the random structure searching, and then increased to 2993 eV for recalculating detailed enthalpy vs. pressure curves. For Brillouin-zone sampling, $14 \times 14 \times 14$ k -points were used for the random searching and then significantly increased for recalculating enthalpy curves. While both

the plane-wave cutoff and number of k -points may seem exceedingly high, such values were found necessary to ensure convergence of each structure to better than 1.5 meV/proton in energy and the pressure to better than 0.1 GPa/proton. Phonons were calculated using density functional perturbation theory. Typical relaxations included at least 100 random structures at each pressure considered. In most cases this appeared to be enough to generate the low-enthalpy structure(s) multiple times. At pressures where the results were considered inconclusive (e.g., a low-enthalpy structure generated only once or twice), additional relaxations were performed. Note that herein we will refer to each structure by its Hermann–Mauguin space-group symbol (international notation), but will also provide more common lattice names, where applicable.

AIRSS was first carried out for unit cells containing 4 and 6 atoms at pressures from 500 GPa to 4.5 TPa in intervals of 500 GPa. Such relaxations implicitly include searches over unit cells of their factors – i.e., those with 1, 2, or 3 atoms. While structures with unit cells of 5 or more than 7 atoms are certainly possible, they are unlikely to occur based on comparisons with other elemental structures. For example, lithium, the closest element to monatomic hydrogen, has a ground state structure consisting of a 3 atom rhombohedral unit cell with space-group $R\bar{3}m$ [15]. Detailed enthalpy vs. pressure curves were then calculated for each structure found, giving the results in Fig. 1. Note that the enthalpy H shown is relative to the face-centered cubic (fcc) lattice (space-group $Fm\bar{3}m$). Also note that the body-centered cubic (bcc) lattice (space-group $Im\bar{3}m$), which was assumed to be the structure of dense hydrogen originally proposed by Wigner and Huntington [1], is not shown in Fig. 1 for clarity, but it is less stable than fcc by approximately 11 meV/proton over the entire pressure range considered [which increases by a further 60 – 70 meV/proton above 1 TPa when proton zero-point energy (ZPE) is included, as discussed below].

Given that our calculations span a large range in pressures, and also much higher than previously considered, Fig. 1 contains a significant number of structures. Below 500 GPa ($r_s = 1.225$), the most stable structure is the molecular phase $Cmca$, which has previously been predicted by both theoretical calculations [21] and AIRSS [17]. Near 500 GPa, $Cmca$ dissociates into a monatomic body-centered tetragonal structure of space-group $I4_1/amd$ with a c/a ratio greater than unity (e.g., $c/a = 2.588$ at 500 GPa), which is shown in Fig. 2(a). This transition is also consistent with previous calculations [17]. Our searches also generated a corresponding $I4_1/amd$ structure with a c/a ratio less than unity (e.g.,

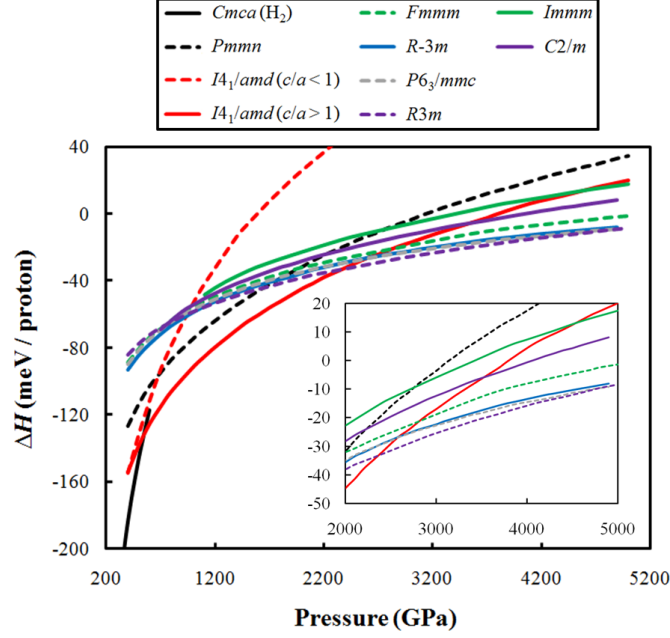


FIG. 1: (color online). Zero-temperature enthalpies of the crystal structures of atomic metallic hydrogen, not including proton ZPE. The inset shows an expanded view of the ultrahigh pressure region.

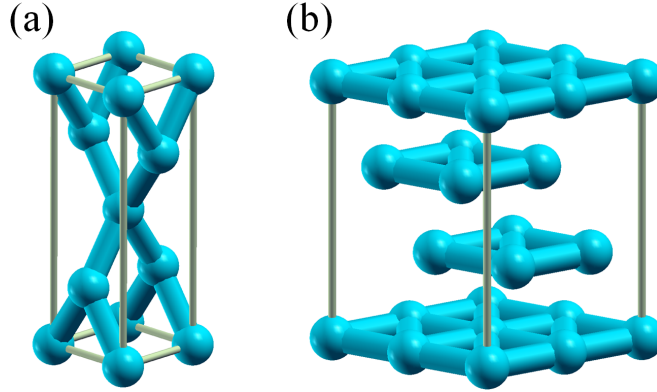


FIG. 2: (color online). Structures of the most stable zero-temperature phases of atomic metallic hydrogen. (a) Unit cell of $I4_1/amd$ ($c/a > 1$) at 1.5 TPa. (b) $2 \times 2 \times 1$ supercell of $R-3m$ at 3.5 TPa. Fictitious bonds have been drawn for clarity.

$c/a = 0.877$ at 500 GPa). However, while both structures are similar in enthalpy near 500 GPa, the latter quickly becomes much less stable with an increase in pressure.

$I4_1/amd$ is found to remain stable until approximately 2.5 TPa ($r_s = 0.969$), resisting compression along the c axis (e.g., $c/a = 2.993$ at 2.5 TPa). This result is similar to

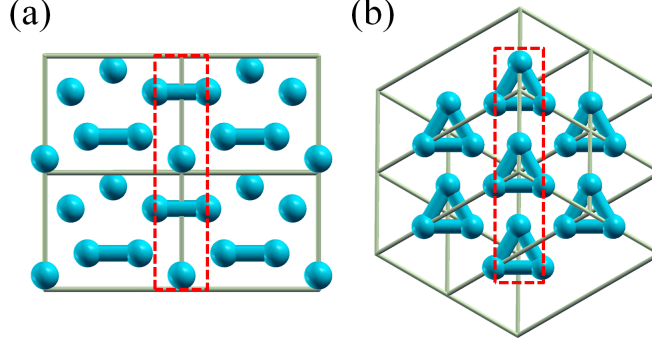


FIG. 3: (color online). Structures of (a) $Pmmn$ at 1.5 TPa and (b) $R3m$ at 3 TPa. Note that the unit cells shown in (b) are actually $2 \times 1 \times 1$ supercells. The dotted lines border linear chains, which stick out of the plane relative to their neighbors.

the conclusion of a previous study that considered a family of tetragonal structures [8]. The only other structure close in enthalpy to $I4_1/amd$ generated during our searches was $Pmmn$, which is still 15 meV/proton less stable over the entire pressure range considered. While relatively unstable, $Pmmn$ does form an intriguing structure. Below 1.9 TPa it is monatomic. However, with increasing pressure a pairing between some atoms occurs forming a mix of molecular and atomic hydrogen that arranges in linear chains; see Fig. 3(a).

Near 2.5 TPa ($r_s = 0.969$) four additional structures with similar enthalpies become important. The least stable is a face-centered orthorhombic structure with space-group $Fmmm$, which is similar to the fcc lattice except elongated along both the b and c axes (e.g., $b/a = 1.724$ and $c/a = 2.021$ at 3 TPa). Both structures are planar, however $Fmmm$ stacks in the sequence $...ABAB...$ whereas fcc does so as $...ABCABC...$ (and is also close-packed). Slightly more stable by 5 – 6 meV/proton are two structures nearly equal in enthalpy. One is $P6_3/mmc$, a hexagonal structure that is also planar with $...ABAB...$ stacking, and is similar to the hexagonal close-packed (hcp) lattice except elongated along the c axis (e.g., $c/a = 2.008$ at 3 TPa). Note that hcp is also of space-group $P6_3/mmc$ with $c/a = 1.633$, and is not shown in Fig. 1 for clarity but is more stable than fcc by about 4.5 meV/proton over the entire pressure range considered (although becomes less stable by 30 – 47 meV/proton when ZPE is included, as discussed below). The other structure is $R\bar{3}m$, a planar structure with $...ABCABC...$ stacking (and with $c/a = 3.028$ at 3 TPa, for example), as shown in Fig. 2(b). (Recall that fcc forms a close-packed version of this stacking sequence, as discussed above.) The most stable structure of this group (by a further 2 – 3 meV/proton at 3.5 TPa,

for example) is $R3m$, which is formed from a rhombohedral unit cell consisting of triatomic molecules; see Fig. 3(b). This structure is likely derived from $Pmmn$ by a compression of the linear chains, followed by a slight distortion.

It is interesting to note that three out of the four structures in this pressure range are anisotropic and planar. This is consistent with previous work that predicted such structures with an increase in density [4, 9]. Similar structures have even been proposed at zero pressure [13]. Perhaps more interesting is that $R-3m$ is also the space-group of the ground state of lithium [15], the structure of which, termed $9R$, differs primarily by its stacking sequence (lithium stacks as $\dots ABCBCACAB\dots$) and packing efficiency. In fact, the $9R$ structure has been previously suggested as a good candidate for the atomic metallic phase of hydrogen [7]. Relative to $R-3m$, however, $9R$ is unstable. This can be inferred by comparing their relative stabilities to bcc. $9R$ is predicted to transform to bcc at 1090 ± 100 GPa [7], while $R-3m$ is stable even above 5 TPa (as it is more stable than fcc; see Fig. 1).

Two additional structures with significantly higher enthalpy were also generated during our searches in the pressure range 2 – 3 TPa, $Immm$ and $C2/m$ (which are qualitatively very similar). Much like $R3m$, these structures are likely derived from $Pmmn$. Below 3 TPa they are very similar to $Pmmn$, comprised of chains of atomic and molecular hydrogen. However, their behavior with increasing pressure is different. $Pmmn$ compresses both along and between the linear chains, forming triatomic molecules connected to their counterparts in neighboring planes. $Immm$ and $C2/m$, on the other hand, resist compression along the c axis, forming molecular chains. It should be noted that such structures have recently been suggested as the ultrahigh pressure ground state of metallic hydrogen [22].

By approximately 4 TPa our searches began generating the “simple” lattices, such as fcc. This suggests that the entire pressure range from 500 GPa to 5 TPa is well mapped out, with the result that the molecular phase ($Cmca$) dissociates into a body-centered tetragonal structure ($I4_1/amd$) near 500 GPa ($r_s = 1.225$), transforming to a planar ($R-3m$ or $P6_3/mmc$) or triatomic ($R3m$) structure near 2.5 TPa ($r_s = 0.969$), which either compresses or transforms to a close-packed lattice (fcc or hcp) above 5 TPa (approximately $r_s < 0.86$).

The scenario outlined above is based on lattices of infinitely massive protons. It therefore actually describes the isotopes of hydrogen with heavier nuclei, including tritium and possibly deuterium. The light proton mass, however, causes hydrogen to have a large ZPE, which must be estimated in order to determine the correct ordering of the structures. Accurately

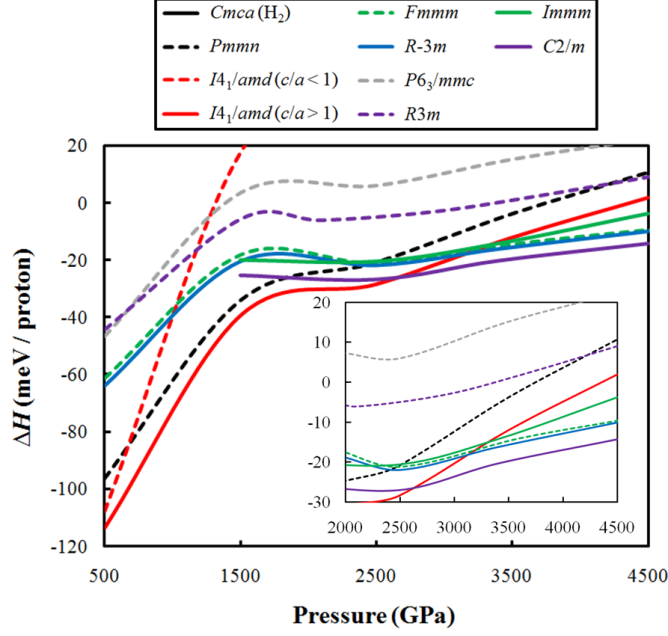


FIG. 4: (color online). Zero-temperature enthalpies of the crystal structures of atomic metallic hydrogen, including proton ZPE. The inset shows an expanded view of the ultrahigh pressure region. Note that a single point representing the molecular phase *Cmca* at 500 GPa is off the scale of the figure, with a relative enthalpy of approximately -132 meV/proton.

estimating ZPE via DFT is particularly challenging because proton zero point motion is anharmonic in atomic metallic hydrogen [2]. A full analysis of these effects is beyond the scope of this work, but some insight can nonetheless be obtained by treating the motion as harmonic.

Phonons were calculated at the Γ point for each structure and the ZPE was estimated in the harmonic approximation: $E_{\text{ZPE}} = (1/2)\hbar\langle\omega_{\text{ph}}\rangle$, where $\langle\omega_{\text{ph}}\rangle$ is the average phonon frequency (which does not include the zero-frequency acoustic modes). Calculating this energy from 500 GPa to 4.5 TPa in intervals of 500 GPa and adding it to the enthalpy in Fig. 1 gives the modified zero-temperature phase diagram shown in Fig. 4. The relative stabilities of the structures are found to drastically change, as expected. For example, while *I41/amd* remains the ground state from 500 GPa to 2.5 TPa, *Pmmn* becomes much closer in enthalpy. At higher pressures, the near degeneracy of *Fmmm*, *P63/mmc*, *R-3m*, and *R3m* is lifted. *R-3m* becomes the clear ground state of this group, followed by *R3m* and *P63/mmc* at much higher enthalpy, while *Fmmm* appears especially unstable. This is not to say that *R-3m* is necessarily the ground state, as *Immm* and *C2/m* become comparable in enthalpy.

It is interesting to note that both ...*ABAB*... planar structures (*Fmmm* and *P6₃/mmc*) become relatively unstable, while the ...*ABCABC*... one (*R-3m*) does not, considering that the major difference is the stacking sequence. Before leaving this topic, it is again worth stressing that proton zero point motion is anharmonic [2], and therefore definitive conclusions regarding the ordering of the structures should not be made even on the basis of Fig. 4.

Because such a large pressure range was considered, it is possible that our searches could have missed some structures. An indication of this as well as possible structure instabilities is given by the appearance of imaginary phonon frequencies. However, it turns out that most of the structures do not exhibit such frequencies over their respective ranges of importance (e.g., *I4₁/amd* and *Pmmn* below approximately 2.5 TPa). Although, both *Immm* and *C2/m*, which become comparable in enthalpy to *R-3m* when proton ZPE is included (Fig. 4), are unstable by 2 – 6.5 meV/proton (also estimated in the harmonic approximation) over the entire pressure range considered, while *R-3m* is completely stable. This suggests that *R-3m* is the ultrahigh pressure ground state structure (within the harmonic approximation, as discussed above).

In summary, we performed AIRSS to determine the zero-temperature structures of atomic metallic hydrogen at pressures from 500 GPa to 5 TPa. We estimate that molecular hydrogen dissociates into a monatomic body-centered tetragonal structure near 500 GPa ($r_s = 1.225$), which then remains stable to 2.5 TPa ($r_s = 0.969$). At higher pressures, the most stable phase becomes a hexagonal ...*ABCABC*... planar structure which is similar to the low-temperature ground state of lithium. With increasing pressure this structure compresses, likely with a continuous change to fcc above 5 TPa ($r_s < 0.86$), analogous to the situation proposed in Ref. [14]. An estimation of the proton ZPE was given in the harmonic approximation. However, a more detailed study including anharmonic effects is necessary to determine the precise ordering of the structures. The fact that we found a significant number of structures at zero-temperature with similar enthalpies suggests that most (if not all) of them will become important at finite temperature, when entropic effects are relevant. A study of the effects of both anharmonicity and temperature is currently underway using coupled electron-ion Monte Carlo [23].

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